Combustion, Explosion, and Shock Waves, Vol. 42, No. 6, pp. 672–677, 2006

Analysis of Flame Structure by Molecular-Beam Mass Spectrometry Using Electron-Impact and Synchrotron-Photon Ionization

Ph. R. Westmoreland,[1] M. E. Law,[1]
T. A. Cool,[2] J. Wang,[2] A. McIlroy,[3]
C. A. Taatjes,[3] and N. Hansen[3]

UDC 536.43, 621.384.8, 537.56, 539.144.7

Translated from *Fizika Goreniya i Vzryva*, Vol. 42, No. 6, pp. 58–63, November–December, 2006.
Original article submitted May 23, 2006.

Molecular-beam mass spectrometry (MBMS) has proven to be a powerful tool for the general analysis of flame structure, providing concentrations of radical and stable species for low-pressure flat flames since the work of Homann and Wagner in the 1960's. In this paper, we will describe complementary measurements using electron-impact ionization with a high-mass-resolution quadrupole mass spectrometer and vacuum-ultraviolet photoionization in a time-of-flight mass spectrometer. Isomers are resolved that have not been separately detectable before in MBMS studies of flames, including C_3H_2, C_3H_4, C_4H_3, C_4H_4, C_4H_5, C_6H_6, and C_2H_4O. The qualitative and quantitative results of MBMS have led to advances in modeling and applying flame chemistry.

Key words: flame structure, mass spectrometry, ionization, synchrotron radiation, isomers.

INTRODUCTION

Molecular-beam mass spectrometry is quite useful in studying flames. First, it is general relative to spectroscopic techniques. Both stable species and radicals may be detected, and many can be identified specifically using molecular weight and ionization energy. Second, sampling along the axis of flat flame gives mole fraction profiles of the species. Such data can be used to test flame models. Third, we can obtain the net rate of reaction at each position. With this information, we can obtain certain rate constants to construct and improve reaction mechanisms.

A truly one-dimensional laminar flame would be a useful experiment for modeling. Suppose that a large box was filled with a combustible fuel–air mixture. Sudden ignition at the entire wall would form a flame that would propagate uniformly into the unburned mixture as heat and hydrogen atoms diffuse rapidly into it. If this system is adiabatic, the temperature of the burned gases would rise to a thermodynamically calculable adiabatic flame temperature. The fuel and oxygen would decrease in mole fraction through the flame front, intermediate species rise and fall, and products rise to a final level. The front would propagate at an adiabatic flame velocity that is characteristic of the fuel, the mixture, the pressure, and the temperature of the unburned gas.

The practical approximation of this ideal is the burner-stabilized flat flame. Premixed gases are fed through a drilled or sintered metal burner. The flame is ignited, and the flame propagates through the flowing gas until it is arrested against the burner. There it will remain at steady state so long as the flow and the pressure are constant. Radially uniform flow rate and cooling of the burner keep radial gradients small near the burner. By using low pressures (20–75 torr),

[1]University of Massachusetts Amherst, Department of Chemical Engineering, Amherst, MA 01003, USA; westm@ecs.umass.edu.
[2]Cornell University, School of Applied and Engineering Physics, Ithaca, NY 14853, USA.
[2]Sandia National Laboratories, Combustion Research Facility, Livermore, CA 94551-0969, USA.

the flame thickness is expanded inversely with respect to pressure, so it can be sampled.

For many years, combustion chemists have successfully mapped composition in flat flames using molecular-beam sampling and quadrupole mass spectrometry with electron-impact ionization, but resolution of hydrocarbon isomers has often proved elusive. Threshold measurement of ionization energy identifies single or dominant isomers easily. By contrast, if isomers are present, energy distribution of the ionizing electrons forces a requirement that ionization energies of the isomers must be more than 2 eV apart for them to be distinguished. This resolution is dramatically improved to 0.1 eV or less by a new alternative, use of vacuum-ultraviolet photons from the advanced light source (ALS) synchrotron at Lawrence Berkeley National Laboratory.

APPARATUS AND PROCEDURE

The two systems both sample low-pressure flat flames, one-dimensional flames that are stabilized against cooled porous flameholders (60.3-mm-diameter McKenna burners) in a laminar flow of premixed fuel, oxidant, and usually an inert diluent like Ar. The flame will remain at steady state so long as the flow and the pressure are kept precisely constant. Radially uniform flow rate and cooling of the burner keep radial gradients small near the burner. By using low pressures 20–75 torr, the flame is expanded to a sufficient thickness for sampling, typically a 10-mm primary reaction zone. Temperature profiles are measured by radiation-compensated, Y_2O_3–BeO-coated, Pt/Pt–15% Rh thermocouples or by optical methods. The small deviation of flow cross-section is measured as an "area expansion ratio" relative to the burner flow area, a function of distance from the burner.

In the MBMS system at the University of Massachusetts Amherst (Fig. 1a), the burner is moved vertically (on the flow axis) and horizontally (radially) with respect to a 40°/90° hybrid sampling probe of the Biordi type [1]. The sampled gases are collimated to a molecular beam with a skimmer nozzle, chopped with a toothed wheel, and introduced into an electron-impact ionizer. The electron-impact ionizer has an energy spread of about 0.7 eV, adequate for distinguishing isomers with threshold ionization energies different by 2 eV or more. The quadrupole mass spectrometer (ABB Extrel) can resolve masses in three different ranges: m/z = 1–50 daltons (ultra-high resolution of $m/\Delta m = 1000$), 1–500, and 4–2000. Positive and negative ions can be measured from radicals and molecules with analog (continuous) or pulse-counting detection. Its advantages are greater sensitivity for weak signals, sufficient mass resolution to resolve oxygenates from hydrocarbons, and established, successful methods for mapping and calibrating flame species.

Ionization by single vacuum-ultraviolet photons has been an appealing but challenging alternative for some time. Lamp sources with cut-off filters were used by Slagle, Gutman and co-workers [2] to measure C_2H_3, CHO, and CH_2O from a pulsed-photolysis flow reactor, yielding kinetics and establishing the latter two species as principal products of $C_2H_3 + O_2$. More recently, McIlroy and co-workers [3] used a frequency-tripled Nd : YAG laser for ionization in a time-of-flight mass spectrometer to analyze flame species. However, lamp/filter approaches are not smoothly tunable, and the lasers may be tuned only through a narrow range. The short, high-intensity laser pulses are also too intense, which can induce photofragmentation and multiphoton ionization.

In the ALS system (Fig. 1b), the unchopped molecular beam is ionized by 10^{14} photons/sec ranging from 5.0 to 24 eV, routinely resolvable to $E/\Delta E = 400$ by a monochromator. This resolution corresponds to ± 0.025 eV at 10.00 eV, so resolution of isomers becomes limited mainly by their photoionization (PI) cross-sections, not the resolution of the ionization source. A 1.3-m time-of-flight mass spectrometer separates the ions, which are detected by a multichannel plate. Advantages are the low photon energies necessary for single-photon ionization, the wide range of electron energies relative to tunable lasers, and much more precise PI energy resolution relative to electron impact. The apparatus is described more completely by Cool et al. [4].

The most valuable feature of the ALS apparatus is spectroscopic resolution of the photons, where the high photon flux compensates for the reduction of photon flux by the monochromator. Species identification and the improved resolution are illustrated dramatically in Fig. 2. Figure 2a shows the electron ionization efficiency measurement for $m/z = 1$ (H^+). Convolution of the thermal energy distribution of the electron-impact filament source with the ionization efficiency effectively causes a shift in the threshold. Calibrating the electron-energy scale against the known ionization energy for H_2 gives a linear shift of +4.6 eV. Extrapolation of the straight-line section to zero signal gives a shift-corrected threshold of (13.7 ± 0.2) eV, compared to 13.595 eV for the literature threshold of H-atom ionization. Note the onset of H^+ from fragmentation at about 18.4 eV (23 eV on the raw scale), which dictates that measurement must be carried out at lower energies to see only

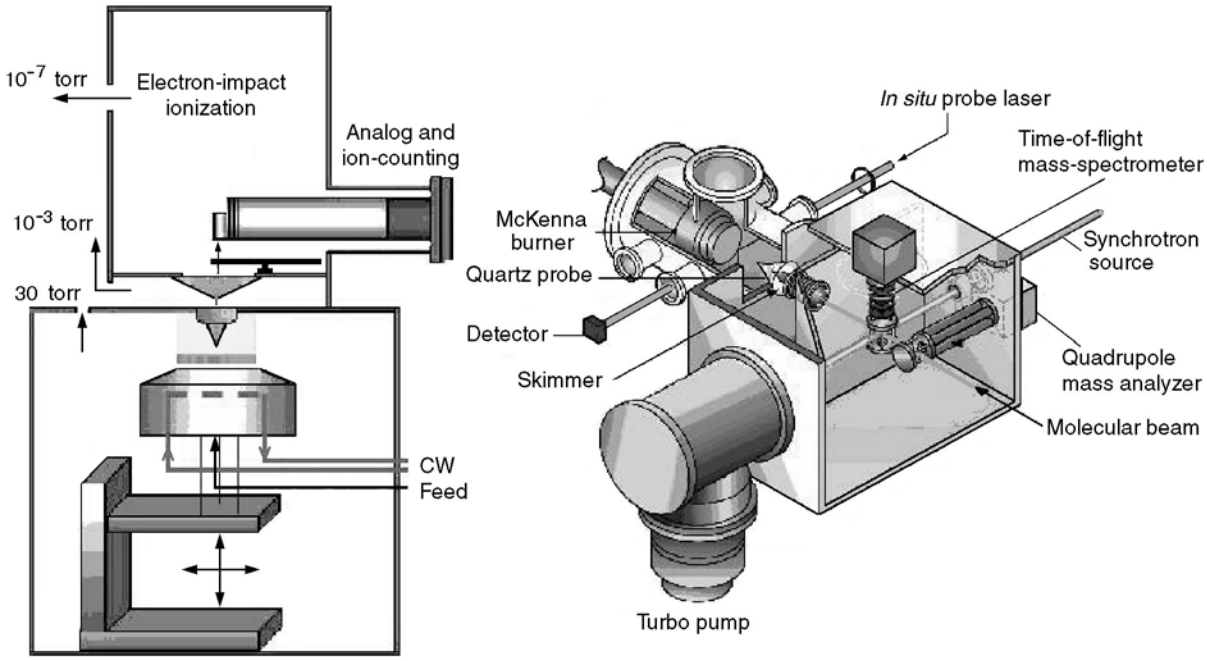

Fig. 1. Schematic drawings of flame-sampling MBMS systems at the University of Massachusetts Amherst (left) and the advanced light source of Lawrence Berkeley National Laboratory (right).

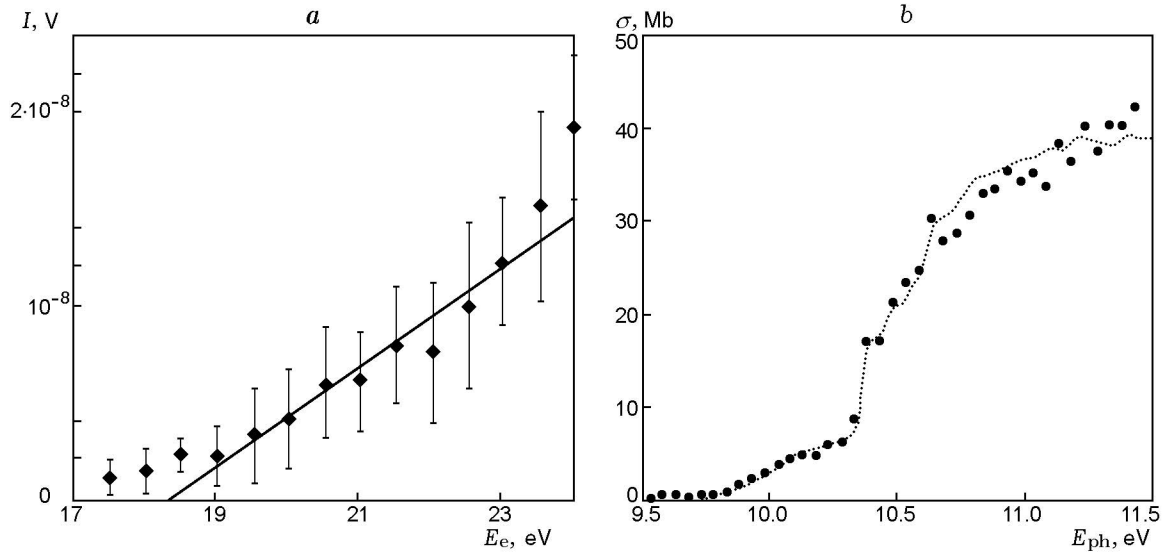

Fig. 2. Experimental ionization-efficiency curves for electron ionization giving $m/z = 1$ (H^+) in a stoichiometric $C_2H_4/O_2/Ar$ flame (a) and photoionization of $m/z = 40$ ($C_3H_4^+$) at 5.0 mm from the burner in a fuel-rich ($\phi = 1.8$) $C_3H_8/O_2/Ar$ flame [7]: (a) the line is a least-squares fit of points for $E_e = 19$–23 eV; (b) the line is a fit of pure-species cross-sections [σ in Mb (megabarn); 1 Mb $= 10^{18}$ cm^2] for allene (ionization potential of 9.692 eV [6]), and propyne (ionization potential of 10.36 eV [6]), giving their C_3H_4 fractions as 0.42 ± 0.05 and 0.58 ± 0.05, respectively.

H^+ from H atom. By contrast, photoionization gives better than an order-of-magnitude better resolution of energies. Figure 2b shows the resolution of C_3H_4 isomers, which is discussed later in this paper.

A necessary correction is accounting for isotopic contributions of lower-mass species. ^{38}Ar and species containing ^{17}O, ^{18}O, ^{13}C, and ^{2}H add their contributions to signals from species of interest. For example, compared to data for acetylene of molecular weight 26 ($^1H^{12}C^{12}C^1H$), there will be a statistical contribution at mass 27 from $^1H^{13}C^{12}C^1H$ and $^2H^{12}C^{12}C^1H$ that is approximately 2.2% of the mass 26 acetylene data. This contribution must be subtracted from the mass 27 data to obtain signal due to vinyl radical ($^1H^{12}C^{12}C^1H_2$). For a C_{16} hydrocarbon like pyrene, the contribution builds to 100 : 18 : 1.5 : 0.1 for masses 202, 203, 204, and 205. For a series of contributions like CH, CH_2, CH_3, and CH_4 and O, OH, and H_2O, each species' contribution must be subtracted in turn, an important consideration for heavier species. Because of mass discrimination and the variation of contributions with varying C/H ratio, it is preferable to use calibrated isotopic ratios from measurements on pure stable species in the MBMS apparatus.

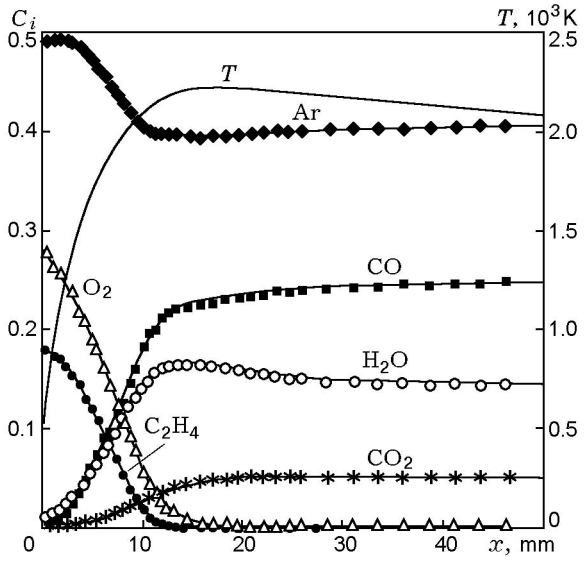

Fig. 3. Temperature and selected major species mole fractions in a fuel-rich $C_2H_4/O_2/50\%$ Ar ($\phi = 1.90$) flat flame for a pressure of 2.666 kPa. MBMS measurements were by electron ionization in the University of Massachusetts Amherst system [5].

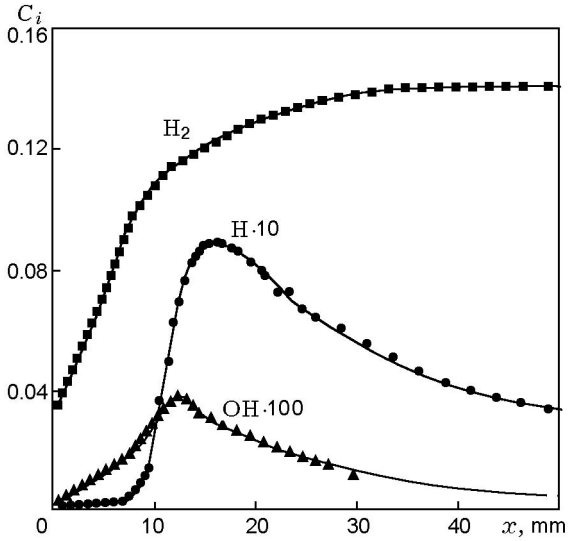

Fig. 4. Mole fractions of H_2, H, and OH in the fuel-rich $C_2H_4/O_2/50\%$ Ar ($\phi = 1.90$) flat flame for a pressure of 2.666 kPa.

DISCUSSION AND CONCLUSIONS

The key data from MBMS measurements are species identities and mole fraction profiles. For modeling and analysis, it is also necessary to measure a temperature profile and an area-expansion profile. Conventional MBMS measurements of profiles will be discussed before turning to the specific opportunities and challenges of synchrotron photoionization.

Ability to quantify a wide range of free-radical and stable species is a signature strength of flame-sampling MBMS. Species are resolved by mass and sometimes by ionization energy.

Example from Electron-Ionization MBMS. Consider selected mole fraction profiles from a fuel-rich C_2H_4 flame [5] as examples of MBMS measurements (Figs. 3–5). For each species, an ionization efficiency curve like that in Fig. 2 was measured in the flame to identify the species by its ionization threshold and to establish an electron energy for profile measurement that would give the maximum signal strength without any interference from fragmentations to or from the species of interest.

In this flame, there is a 90% excess of C_2H_4 relative to stoichiometric conversion to H_2O and CO_2, so CO and H_2 are major products. Temperature quickly rises to a maximum of 2200 K and then slowly declines in the post-flame zone. Note that the mole fraction of argon is not constant but declines and then rises slightly. This variation is because of the changing number of moles due to reaction of other species. Also, while C_2H_4 and O_2 mole fractions are declining beginning at the burner surface, their mass fluxes are initially constant; their mole fractions decrease initially because

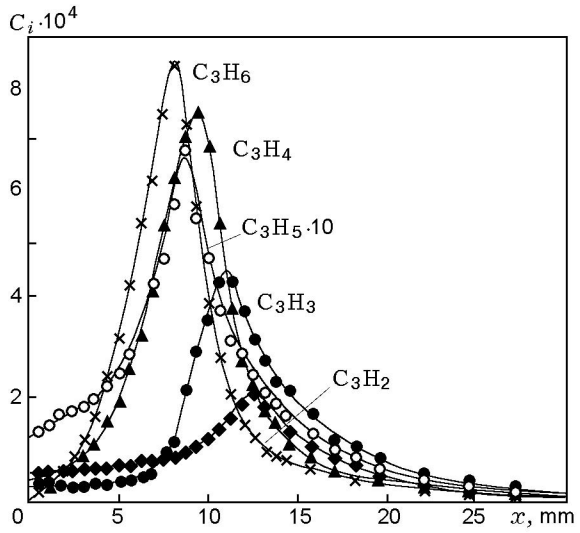

Fig. 5. Mole fractions of C_3 molecules and radicals in the fuel-rich $C_2H_4/O_2/50\%$ Ar ($\phi = 1.90$) flat flame for a pressure of 2.666 kPa.

of back-diffusion of flame intermediates, not because of reactions.

"Isomers" like CH_2CO and C_3H_6 ($m/z = 42$) can be resolved by mass difference if accessible resolution of the mass spectrometer is sufficiently high. In the study of Figs. 3–5, a moderate mass resolution left O atom ($m/z = 16.00$) obscured by the strong signal from CH_4 ($m/z = 16.04$). From modeling, maximum O mole fraction was estimated to be quite low, reaching only about $5 \cdot 10^{-6}$. This mass spectrometer has since been upgraded to one with much higher mass resolution, and CH_4 and O are now resolved routinely in the apparatus.

In contrast, true isomers cannot be resolved by masses alone, and ionization energy may be used as another basis for separation. Resolution by ionization thresholds is easy even at unit mass resolution for some species. For example, C_2H_4 has an ionization energy of 10.5138 eV and mass 28.05, while CO has 14.014 eV and mass 28.01. The difference of 3.5 eV is sufficient to give a strong signal for C_2H_4 in the linear region of its ionization efficiency curve, free from interference by CO. This signal is extrapolated to 16.4 eV using the pure-C_2H_4 ionization efficiency measurement and subtracted from the total mass 28 signal, leaving the signal due to CO.

Precise Resolution by Synchrotron Photoionization. Ionization energies of the C_3H_x isomers (Fig. 4) are too close to be resolved by electron ionization. Ionization energies of the C_3H_4 isomers are 9.67 eV (cyclopropene), 9.692 eV (1,2-propadiene or allene) and 10.36 eV (propyne); all are easily resolved from Ar at 15.759 eV [6]. Cyclopropene was ruled out as a major contributor because it is 92 kJ/mole higher in energy (ΔH^0_{298}) than the lowest-energy isomer, propyne. Allene is only 5.5 kJ/mole higher and so should be present, and in some cases, we add small amounts of allene into the C_2H_4 feed flow. As shown in Fig. 2, the precise resolution of ionizing-photon energies provided very clean resolution of allene and propyne. The resolved isomers were quantified into separate profiles by using measurements of the pure-species cross-sections, as detailed by Cool et al. [7]. Similarly, C_3H_2 was identified as triplet propargylene and/or singlet cyclopropenylidene [8], and C_3H_3 was confirmed as propargyl.

This paper describes how the new application of spectroscopically resolved photons from a synchrotron (the LBNL ALS) is applied to advance the power of MBMS dramatically.

We gratefully acknowledge support of this work by the U.S. Department of Energy, Office of Basic Energy Sciences [Grant Nos. DE-FG02-91ER14192 (M.E.L. and P.R.W.) and DE-FG02-01ER15180 (J.W. and T.A.C.)] and by the Chemical and Biological Sciences Division of the U.S. Army Research Office [Contract No. C-DAAD19-00-1-0099 (T.A.C)]. Sandia (A.M., C.A.T., and N.H.) is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.

REFERENCES

1. J. C. Biordi, C. P. Lazzara, and J. F. Papp, "Molecular beam mass spectrometry applied to determining the kinetics of reactions in flames. I. Empirical characterization of flame perturbation by molecular beam sampling probes," *Combust. Flame*, **23**, 73 (1974).
2. I. R. Slagle, J.-Y. Park, M. C. Heaven, and D. Gutman, "Kinetics of polyatomic free radicals produced by laser photolysis. 3. Reaction of vinyl radicals," *J. Amer. Chem. Soc.*, **106**, No. 16, 4356 (1984).
3. A. McIlroy, T. D. Hain, H. A. Michelsen, and T. A. Cool, "A laser and molecular beam mass spectrometer study of low-pressure dimethyl ether flames," *Proc. Combust. Inst.*, 1647–1653 (2000).
4. T. A. Cool, A. McIlroy, P. R. Westmoreland, et al., "A photoionization mass spectrometer for studies of flame chemistry with a synchrotron light source," *Rev. Sci. Instrum.*, **76**, 094102-1–094102-7 (2005).

5. A. Bhargava and P. R. Westmoreland, "Measured flame structure and kinetics in a fuel-rich ethylene flame," *Combust. Flame*, **113**, 333–347 (1998).
6. S. G. Lias, "Ionization energy evaluation," in: P. J. Linstrom, W. G. Mallard (eds.), *Chemistry WebBook*, Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg (2005); http://webbook.nist.gov.
7. T. A. Cool, K. Nakajima, T. A. Mostefaoui, et al., "Selective detection of isomers with photoionization mass spectrometry for studies of hydrocarbon flame chemistry," *J. Chem. Phys.*, **119**, No. 16, 8356–8365 (2003).
8. C. A. Taatjes, S. J. Klippenstein, N. Hansen, et al., "Synchrotron photoionization measurements of combustion intermediates: photoionization efficiency of C_3H_2 isomers," *Phys. Chem. Chem. Phys.*, **7**, 806–813 (2005).